Rapid Reactions. The Velocity and Heat Effects Involved in the Neutralization of Sodium Dichromate

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DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE COLUMBIA UNIVERSITY

By

Chester L. Read, B.S., Ch.E., M.A.

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RAPID REACTIONS.
THE VELOCITY AND HEAT EFFECTS INVOLVED IN THE NEUTRALIZATION OF SODIUM DICHROMATE BY SODIUM HYDROXIDE

1. Introduction

Various investigators have endeavored to study some of the more rapid reactions but little has been accomplished in this field until comparatively recently. Abegg and Neustadt[1] tried to follow the reaction between H^+ and OH^- in alcoholic solutions at low temperatures. It is quite probable that the reported time of the reaction, one-half to two minutes, was the time required for the solutions to mix at that temperature. Benedicks[2] used similar solutions at room temperature and attempted to follow the rate of reaction by conductivity methods. Round holes were cut in two glass plates and each hole was fitted with an electrode. One of the reacting solutions was placed in each of the cavities and the plates were moved so that the holes were rapidly brought opposite each other. The conductivity of the resulting solution was recorded continuously by mechanical methods. It was found that two-tenths of a second was required for complete mixing of the solutions, while the reaction reached completion in a much shorter time.

The first comprehensive study of a rapid reaction was made by Hartridge and Roughton[3] when they applied their flowing stream method to a reaction involving hemoglobin. The principle of the method consisted in causing the solutions whose reaction is to be studied to come together at high velocity in a mixing chamber where they are rapidly and completely mixed. The resulting solution then passes through a reaction tube where the progress of the reaction is observed. With constant velocity maintained through the tube, the time required for the mixed solution to reach a given point is constant and consequently the reaction is always in the same state when the solution reaches this point. Various methods may be used to follow the progress of the reaction; in most of the work reported by Hartridge and Roughton the spectroscope was used. In their most highly de-

[1] Abegg and Neustadt, *Z. Elektrochem.*, **14,** 2 (1908).

[2] Benedicks, *Z. physik. Chem.*, **70,** 12 (1910).

[3] Hartridge and Roughton, (a) *Proc. Roy. Soc.*, (London) **A104,** 376 (1923); (b) *Proc. Camb. Phil. Soc.*, **22,** 426 (1925); (c) *ibid.*, **23,** 450 (1926).

veloped apparatus, the first reading could be taken $^1/_{6000}$ second after mixing. Although most of their work was along biological lines, the reaction between 0.1 normal solutions of hydrochloric acid and sodium hydroxide was studied and found to be complete in less than 0.001 second.[4]

Saal[5] used an apparatus of this type applying conductivity and e. m. f. methods to follow the reactions. He attempted a survey of the different types of reactions taking place between electrolytes and concluded that "ionic reactions in which there is no change of charge and in which no secondary reactions having a fundamental influence on the ion or molecule occur, are complete to 1% within 0.004 second" and that "oxidation and reduction reactions are usually slow."

In this research, the apparatus used was similar to that of Hartridge and Roughton except that the reactions were followed by means of thermocouples which measured the temperature change due to the heat of reaction evolved.

2. Apparatus

A schematic diagram of the apparatus is given in Fig. 1. Air, at constant pressure, is applied to the two sets of bottles C and D through the regulating valve A. The applied pressure is given by the manometer B. The two solutions are forced through glass tubes to the mixing apparatus E. Detailed views of the mixing apparatus are given in Fig. 2. It consists of two square gold-plated brass plates which are bolted together. Each plate contains a circular header, I and J, of square cross section, the outer diameter being 85 mm., the inner 45 mm. and the depth 15 mm. Each header is fed by two tubes; solution from bottles C and C′ enters header I by the tubes G and G′ while the solution from D and D′ enters header J by means of the tubes H and H′. The solutions pass from the headers to the jets by means of sixteen holes, eight being drilled symmetrically through each plate. In the cross section view, two of the holes are indicated as K. All of the holes in the back plate are designated in a similar manner in the view of the face of the rear plate. The solution from C and C′ passes through the header I and the holes K into eight alternate jets. These jets are 1 mm. deep and at the entrance to the mixing chamber they are approximately 1 mm. wide. The mixing chamber L is 12 mm. in diameter and 1 mm. deep and approximately of 0.1 cc. volume. The solutions enter it at high velocity and in a direction tangent to the outer edge. The swirling motion produced results in rapid mixing. The mixed solutions pass into the reaction tube M which is a hard rubber tube of 6.35 mm. bore. Thermocouple junctions, mounted on hard rubber pegs as N, are placed at intervals along the reaction tube. The first junction, which is not shown in the sketch, is 1 mm. from the mixing chamber. The cold or reference junction O is mounted on a hard rubber screw, the junction being in the center of the mixing chamber.

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[4] The continuous flow principle of calorimetry has been employed previously by Pratt, *J. Franklin Inst.*, **185,** 663 (1918), for the determination of heats of dilution of aqueous solutions and by Keyes and Dickinson [Thesis, Massachusetts Institute of Technology, **1917,** referred to by Keyes, Gillespie and Mitsukuri, THIS JOURNAL, **44,** 707 (1922)] for the determination of heats of neutralization. Bray and Livingston, *ibid.*, **50,** 1654 (1928), have also employed a flowing stream method but for the very much slower reaction between hydrogen peroxide and bromine.

[5] Saal. *Rec. trav. chim.*, **47,** 73, 264, 385 (1928).

Flow of Solutions.—It is essential that the rate of flow of the mixed solution through the reaction tube be as nearly constant as possible while a set of readings is being taken and also that this solution be composed of equal volumes of the reacting solutions.

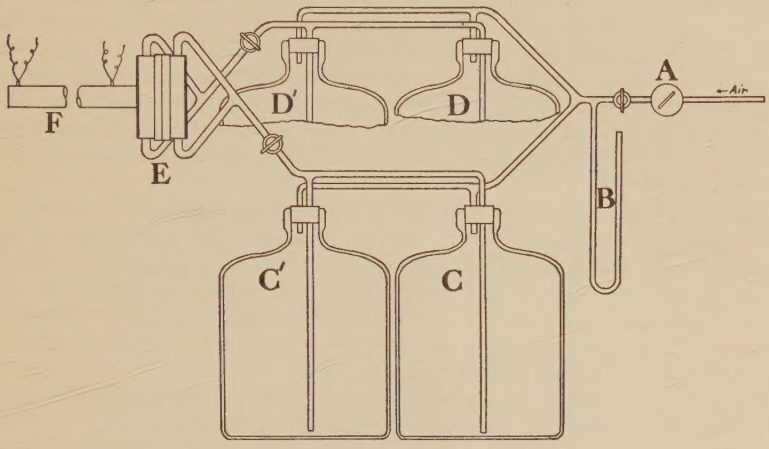
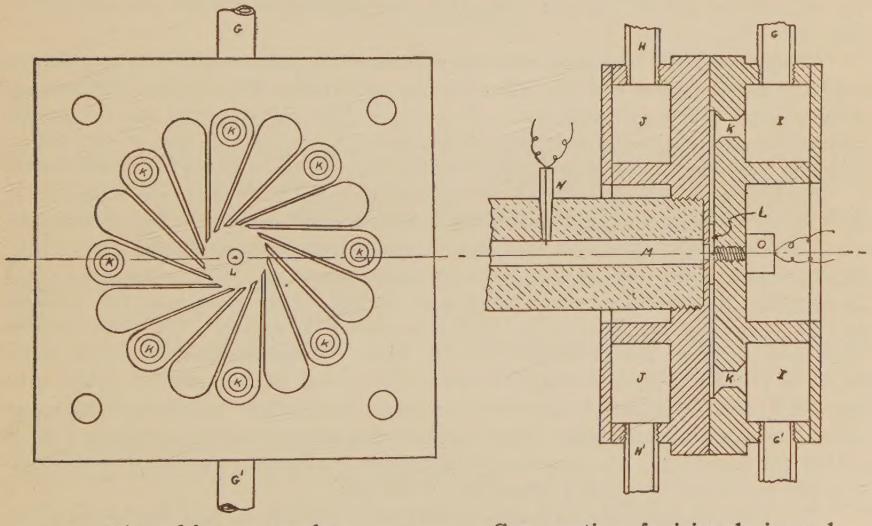


Fig. 1.—Schematic diagram of apparatus.

The rate of flow through the apparatus is approximately proportional to the square root of the pressure applied, so small changes in pressure do not greatly influence the rate of flow. This is especially true when high pressures are applied. The pressure could be



View of face—rear plate.

Cross section of mixing device and reaction tube.

Fig. 2.

easily regulated and the fluctuations during an entire run were less than 1 mm. of mercury. Bottles of large cross section containing 36 liters of each solution were used in order that there might be little change in the level of the solutions during a run and con-

sequently little change in the effective pressure applied to them. The variations in flow were less than 1% during a half hour period.

In each system the solution containers and the connections to the mixing apparatus were as nearly identical as possible in order that the liquid levels might remain the same in all four bottles and that each system might offer the same resistance to the flow of the liquid. Several methods were used to determine the ratios of rates of flow in the two systems under various conditions. The stopcock on one side was closed and the rate of flow through the other system was determined for various pressures. This side was then closed off and the rate of flow through the other system was determined. The rates of flow for each side for a given pressure checked within the limit of accuracy for this measurement, $\pm 0.5\%$.

One set of bottles was filled with 0.05 *N* hydrochloric acid and the other set with sodium hydroxide of equal strength. Various pressures were applied to the bottles and the stopcocks were adjusted for each pressure so that the greatest possible temperature rise between the mixing chamber and a given junction was obtained. This would occur when the reacting solutions were present in equal concentration. This condition always existed when the stopcocks were wide open. Under these conditions the solution leaving the reaction tube was neutral to litmus paper.

For any set of readings the variation in rate of flow was not greater than 1% and the variation in concentration of the reacting solution was less than 0.5%.

Thermocouples.—Copper–constantan thermocouples of No. 30 wire were used. A Leeds and Northrup type HS galvanometer could be connected between the cold or reference junction and any of the hot junctions by means of a series of switches. The galvanometer was connected in the copper side of the thermocouple circuit and all contacts were of copper in order to eliminate thermal effects. The galvanometer setting, the switchboard and the reaction apparatus were shielded to provide protection from stray currents.

The galvanometer was mounted on the wall above the apparatus and 1.5 meters from the lamp and scale used with it. The temperature difference between two junctions was obtained directly from the deflection. The period of the galvanometer was 7.5 seconds and by having the external resistance in the circuit approximately that of the critical damping resistance of the instrument, a reading could be taken in ten to fifteen seconds.

Each thermocouple junction of the set used gave the same deflection within 0.1% for a given temperature gradient between it and the cold junction. Before installing the junctions in the apparatus they were connected to the switchboard and the galvanometer was calibrated over the desired temperature range. This was accomplished by attaching the cold or reference junction to the bulb of one Beckmann thermometer and the remaining junctions to the bulb of a second Beckmann. The thermometers were then placed in Dewar flasks filled with water at room temperature. The water in the first flask was gradually cooled so that after several hours it was 0.5° colder than the water in the other flask. Readings were taken at short intervals of the temperature difference between the contents of the two flasks and the corresponding deflection given by the galvanometer. The temperature–deflection relationship was linear, a temperature differential of 0.1° giving a deflection of 7.225 cm.

The thermocouple junctions were coated with bakelite varnish and mounted on conical pegs, the wires being fitted into small grooves on opposite sides of the pegs. The remaining space in the grooves was filled with varnish. The peg was fitted into a hole in the reaction tube at a measured distance from the mixing chamber. It was found that when there was an appreciable temperature differential between the reaction solution in the reaction tube and the thermocouple wires going from the tube, heat was conducted to or from the junction and the true temperature differential between this point and

the mixing chamber was not recorded. Much of this error was eliminated by winding 20 to 25 cm. of the copper and constantan wires, adjacent to the junction, around the reaction tube and then giving the whole apparatus a heavy coating of paraffin.

The first three junctions (not shown in Fig. 2) were placed so close together and so close to the end of the tube that it was not possible to mount them on pegs. Two narrow slits were cut in the tube and the wires were run through these slits. The junctions were held in place by means of bakelite varnish.

Nine junctions were placed in the reaction tube, the distances from the front end of the tube being 1, 4, 10, 20, 50, 100, 250, 500 and 1000 mm. When the rate of flow of the reacting solutions through the tube was 50 cm. per second, the first reading was taken 0.004 second after mixing and the last reading, 2.00 seconds after mixing. When the rate of flow was 100 cm. per second, the corresponding times were just half these values.

The reference junction O was mounted on a hard rubber peg which screwed into the back plate of the mixing apparatus in such a manner that the junction was in the middle of the mixing chamber. Junctions were also placed in the tubes leading to the mixing apparatus in order to determine the temperature difference between the solutions entering the apparatus.

Temperature Control.—The four 18-liter bottles containing the solutions were kept in a large water thermostat regulated to 25 ± 0.005°. The solutions were placed in the thermostat at least twenty-four hours prior to a run to allow ample time for them to reach the temperature of the bath. The reaction apparatus was mounted in a wooden tank and water from the thermostat was circulated through it. The rate of circulation was rapid and the tank capacity small in comparison with that of the thermostat. The temperature of the tank was maintained within 0.005° of that in the thermostat. Precise temperature control was found to be essential in securing concordant data.

3. Procedure

Air was applied to the solution bottles and regulated to the desired pressure. The stopcocks were then opened and the solutions allowed to flow through the apparatus. The rate of flow was measured by determining the time required for a given volume of solution to flow from the end of the reaction tube. If the rate of flow was not that desired, the pressure was regulated to give the desired flow. Thermal equilibrium was not reached immediately, so the first temperature readings were taken several minutes after the flow had been regulated. The data recorded for each set of readings consisted of the temperature difference between the two solutions as they entered the mixing apparatus, the temperature differences between the mixing chamber and each of the nine junctions, the air pressure and the rate of flow before and after taking the temperature readings. The first set of temperature readings was usually quite close to equilibrium and this condition was attained within ten minutes. Four or five sets of readings were taken at three- to five-minute intervals after the system had reached equilibrium.

4. Reagents

Analyzed chemicals obtained from J. T. Baker Chemical Co. and from Eimer and Amend were used without further purification. The solutions were made up and standardized against standard solutions. If the con-

centrations were not within 0.3% of that desired, they were adjusted within that limit. The sodium hydroxide contained approximately 0.1% of sodium carbonate and the solutions were standardized against hydrochloric acid solution. The sodium dichromate solutions were standardized against sodium thiosulfate solution.

5. Acid–Base Reactions—Proof of Mixing

The reaction between sodium hydroxide and hydrochloric acid, which was studied by Hartridge and Roughton, was used to check the effectiveness of mixing with this apparatus. The first temperature reading was taken 0.002 second after mixing, and since this reaction is complete in less than 0.001 second, the temperature rise equivalent to the heat of reaction for the complete reaction should be obtained at the first junction, if the mixing is complete at that point. Solutions of hydrochloric acid and sodium hydroxide of 0.05 normal concentration were run through the apparatus, the rate of flow through the reaction tube being 100 cm. per second. The corrected temperature differences between the mixing chamber and each of the junctions in the reaction tube were within 0.004° of 0.340°. Calorimetric data require that this value should be 0.342°.

These results prove that mixing is complete before the first junction in the reaction tube is reached and also that the entire reaction takes place between the cold junction and the first hot junction. It is evident that mixing does not take place until the reacting solutions reach the center of the mixing chamber.

Saal has studied various acid–base reactions, apparently using a strong acid with a weak base or a strong base with a weak acid. He concluded that these reactions are all complete to within 1% in less than 0.004 second. The reaction between a weak acid and a weak base has not been reported, so the reaction between acetic acid and ammonium hydroxide was observed. Using 0.05 normal solutions, it was found that the reaction was 95% complete in 0.002 second and equilibrium was reached in less than 0.01 second. The temperature rise for this reaction was 0.192°. These results indicate that the strength of the acid and base do have an effect on the velocity of neutralization. We intend to study this question in more detail in a later publication using an improved instrument.

An attempt was made to use still weaker acids and bases but the results were not satisfactory. The heat of neutralization is to a large extent offset by the increased heats of ionization, so that unless solutions of high concentration are used, the temperature rise due to the heat of reaction is not much greater than the experimental errors.

6. Neutralization of Sodium Dichromate by Sodium Hydroxide

This reaction is usually written as follows

$$Na_2Cr_2O_7 + 2NaOH \longrightarrow 2Na_2CrO_4 + H_2O$$

It was found to be well suited for study with this apparatus as it reaches equilibrium in one to two seconds and the heat evolved was comparable to that evolved on the neutralization of a moderately strong acid. Sodium dichromate solutions of 0.02, 0.04 and 0.06 molar concentration were neutralized by sodium hydroxide solutions of equivalent concentrations. The results obtained are given in Table I and are represented graphically in Fig. 3, in which the temperature rise between the mixing chamber and a given junction is plotted against the time required for the mixed solution to

TABLE I

ORIGINAL DATA CORRECTED FOR WATER EFFECT

Junction no.	Time, sec.	Temp., °C.	Time, sec.	Temp., °C.
	Curve Ia		Curve Ib	
1	0.004	0.072	0.002	0.071
2	.010	.077	.005	.072
3	.022	.084	.011	.082
2	.042	.098	.021	.093
5	.100	.124	.050	.111
6	.200	.138	.100	.130
7	.500	.149	.250	.151
8	1.000	..	.500	.152
9	2.000	.166	1.000	.169
	Curve IIa		Curve IIb	
1	0.004	0.150	0.002	0.144
2	.010	.156	.005	.148
3	.022	.176	.011	.158
4	.042	.206	.021	.170
5	.100	.269	.050	.220
6	.200	.311	.100	.257
7	.500	.315	.250	.291
8	1.000	.334	.500	.317
9	2.000	.355	1.000	.343

Junction no.	Time, sec.	Temp., °C.	Time, sec.	Temp., °C.
	Curve IIIa		Curve IIIb	
1	0.004	0.202	0.002	0.212
2	.010	.218	.005	.218
3	.022	.255	.011	.232
4	.042	.305	.021	.264
5	.100	.406	.050	.331
6	.200	.472	.100	.417
7	.500	.529	.250	.479
8	1.000	.540	.500	.529
9	2.000	.554	1.000	.564
	Curve IV		Curve V	
1	0.002	0.148	0.002	0.184
2	.005	.152	.005	.186
3	.011	.161	.011	.199
4	.021	.174	.021	.230
5	.050	.209	.050	.306
6	.100	.266	.100	.355
7	.250	.291	.250	.357
8	.500	.332	.500	.360
9	1.000	.355	1.000	.360

reach the junction. Curves I, II and III represent the above-mentioned reactions. Each curve represents two sets of data, the velocity of flow through the reaction tube being 50 cm. per second in one and 100 cm. per second in the other. The "a" curves represent the lower velocity and the "b" curves the higher. These curves do not start from the origin and when extrapolated to zero time have finite intercepts.

Curve IV represents the neutralization of 0.04 molar sodium dichromate by 0.16 molar sodium hydroxide, twice the OH^- concentration required. This curve is so similar to II that to add the additional data to the graph would only make it more difficult to identify the points for curves Ia and Ib. These data prove that the velocity of the reaction is not affected by the OH^- concentration.

Curve V represents the partial neutralization of 0.08 molar sodium dichromate by 0.08 molar sodium hydroxide, half the OH^- concentration

required for the neutralization. This curve is quite different from curve II as it rises much more rapidly until the OH^- is used up. These data show that the velocity of the reaction is a function of the concentration of the dichromate ion.

The data for the equilibrium between dichromate and chromate yield an explanation for these curves. Sherrill[6] has investigated the equilibrium between dichromate and hydrochromate by a freezing point method.

$$Cr_2O_7^{=} + H_2O \rightleftharpoons 2HCrO_4^- \qquad K_1 = (HCrO_4^-)^2/(Cr_2O_7^{=})$$

The values of K_1 vary from 0.0145 to 0.0196 over a concentration range of 0.01 to 0.05 molar potassium dichromate. The dissociation of the hydro-

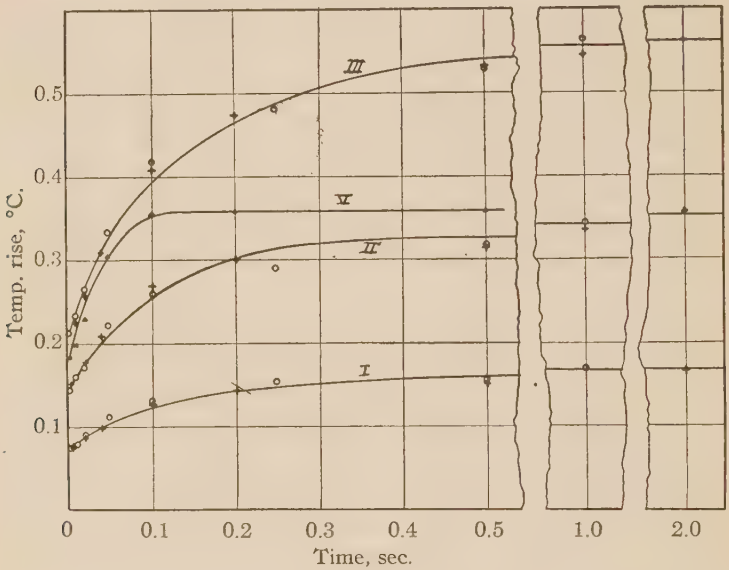


Fig. 3.—Graph of original data.

chromate ion was determined from the hydrolysis of ammonium chromate and also from distribution data.

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{=} \qquad K_2 = (H^+)(CrO_4^{=})/(HCrO_4^-)$$

The values for K_2 are given as 5.2 to 5.9 $\times$ 10^{-7} at 18° and 7.4 $\times$ 10^{-7} at 25°.

Saal has redetermined the value for K_1 by measuring the amount of OH^- required to neutralize rapidly the $HCrO_4^-$ in equilibrium with the $Cr_2O_7^{=}$. He found the value of K_1 to be 0.019 $\pm$ 0.001 for concentrations up to 0.125 molar in potassium dichromate. On the basis of this value of K_1, the concentrations of $Cr_2O_7^{=}$ and $HCrO_4^-$ present in equilibrium in the sodium dichromate solutions used have been calculated and are given in Cols. 5 and 6 of Table II. For the concentration range used in these experiments,

[6] Sherrill, *J. Am. Chem. Soc.*, **29**, 1641 (1907).

approximately one-third of the chromium is present as the hydrochromate. The sudden rise in the temperature–time curves can be explained on the basis of the very rapid reaction between the $HCrO_4^-$ present and the OH^-. This is in agreement with the evidence previously offered that acid–base reactions reach equilibrium in a very few thousandths of a second, even when one of the components has a small dissociation constant.

TABLE II

ANALYSIS OF EXPERIMENTAL DATA

1	2	3	4	5	6	7	8	9
Run no.	Concn. of $Na_2Cr_2O_7$ taken, mole/l.	Concn. of NaOH, mole/l.	Velocity of mixed solns. through R. T., cm./sec.	Concn. of $Cr_2O_7^=$, mole/l.	Concn. of $HCrO_4$, mole/l.	ΔT between M. C. and last junction, °C.	ΔT due to heat of diln. of $Na_2Cr_2O_7$, °C.	ΔT due to heat of neutn., 7 + 8, °C.
Ia	0.02	0.04	50	0.0124	0.0152	0.166	−0.010	0.176
Ib	.02	.04	100	.0124	.0152	.169	−.010	.179
IIa	.04	.08	50	.0284	.0232	.355	−.019	.374
IIb	.04	.08	100	.0284	.0232	.343	−.019	.362
IIIa	.06	.12	50	.0453	.0294	.554	−.021	.575
IIIb	.06	.12	100	.0453	.0294	.564	−.021	.585
IV	.04	.16	100	.0284	.0232	.355	−.019	.374
V	.08	.08	100	.0627	.0346	.360	..	..

10	11	12	13	14	15
Run no.	ΔT, between junctions 1 and 9, °C.	ΔT 10 extrapolated to zero time, °C.	Theoret. ΔT for the reaction had there been no initial hydration of the $Cr_2O_7^=$, °C.	Diff. between actual ΔT and theoret., 9–12, °C.	Heat of reaction $Na_2Cr_2O_7 + 2NaOH \rightarrow 2NaCrO_4 + H_2O$ steps "a" + "b" + "c," cal./mole of $Cr_2O_7^=$	Heat of hydration of $Cr_2O_7^=$ in forming $HCrO_4^-$ Cal./mole of $Cr_2O_7^=$
Ia	0.094	0.097	0.156	0.020	+15,600	(−5270)
Ib	.098	.100	.161	.018	+16,100	(−4740)
IIa	.205	.210	.296	.078	+14,800	−13,500
IIb	.199	.201	.283	.079	+14,150	−13,600
IIIa	.352	.363	.489	.095	+16,000	−12,900
IIIb	.352	.362	.479	.106	+16,000	−14,400
IV	.207	.209	.294	.080	+14,700	−13,800
V	.176	.196	.345	..	.....	.....
					Av., +15,320	Av., −13,640

The mechanism of the reaction between sodium dichromate and sodium hydroxide is postulated to take place in three steps, as follows

$$Cr_2O_7^= + H_2O \rightleftharpoons 2HCrO_4^- \quad (a)$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^= \quad (b)$$

$$H^+ + OH^- \rightharpoonup H_2O \quad (c)$$

The steps "b" and "c" take place in the interval of time between the mixing of the solutions and their reaching the first junction in the reaction tube. From analogy with other hydration reactions step "a" must be slow and this reaction is the one whose velocity is measured. The concentration of the water is large in comparison with that of the $Cr_2O_7^=$ so it would be expected that the rate of hydration would be pseudo-monomolecular and

of the first order in respect to $Cr_2O_7^=$. This is in agreement with the data already presented.

The heat effects of the various steps may be obtained from an analysis of the experimental data give in Table II and a graphic representation of the various items given in Fig. 4. Col. 1 in Table II gives the number of the run, Cols. 2 and 3 the concentrations of the reacting solutions, and Col. 4 the velocity of the mixed solutions through the reaction tube. It will be noted that the "b" curves are duplicates of the "a" curves except that the velocity through the reaction tube is 100 cm. per second instead of 50 cm. per second. Cols. 5 and 6 represent the concentrations of $Cr_2O_7^=$ and $HCrO_4^-$ present in the sodium dichromate solutions. Column 7 gives the temperature rise between the mixing chamber and the last junction in the reaction tube. This item and the succeeding ones are represented in Fig. 4.

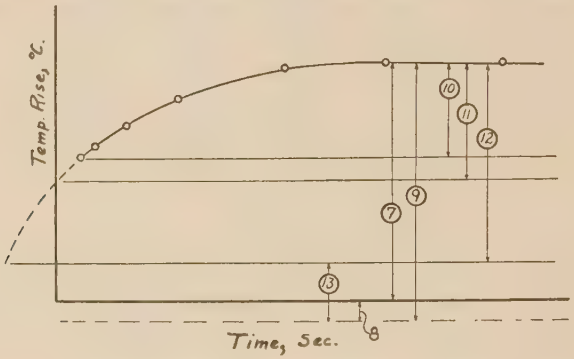


Fig. 4.—Diagrammatic representation of temperatures.

A small correction has been applied to these values to correct for the temperature change due to the friction of water passing through the apparatus. To obtain the temperature rise due to the three steps "a," "b" and "c," the heats of dilution of the reacting solutions must be taken into account. The heat of dilution of sodium hydroxide is quite small and may be neglected. This is not the case with sodium dichromate. The temperature change due to the dilution of the various concentrations of sodium dichromate with equal volumes of water has been determined experimentally by means of the reaction velocity apparatus and these values are given in Col. 8. This correction must be applied to the values given in Col. 7 in order to obtain the true temperature rise due to the steps "a," "b" and "c." This latter value is given in Col. 9.

The temperature rise between junctions one and nine is given in Col. 10. The curves given in Fig. 3 may be extrapolated to zero time. The temperature difference between this intersection with the zero ordinate and the ninth junction is given in Col. 11. This temperature rise is due to the hydration of that concentration of $Cr_2O_7^=$ initially present in the aqueous

solution (Col. 5) and the subsequent neutralization of the $HCrO_4^-$ formed. From this temperature rise and the initial concentration of $Cr_2O_7^=$, the theoretical temperature rise obtainable if there were no initial hydration can be computed. This value is given in Col. 12. It is the temperature rise due to the reactions "a" + "b" + "c," and the heat effect per mole of $Cr_2O_7^=$ can be obtained from this value and the concentration of the sodium dichromate solution. The values for the sum of the heat effects of these three steps are given in Col. 14, the average value being +15,320 ± 675 calories per mole of $Cr_2O_7^=$. In making the calculations for the heat effects no allowance has been made for the reduced specific heat or the increased specific gravity of the solutions due to the presence of the salt. These effects tend to offset each other so that the results given are probably about 1% high for the most concentrated solutions. Sufficient data are not available for the calculation of such a correction and it is of the same order of magnitude as the experimental error.

The theoretical value of the temperature rise for these three steps (Col. 12) is considerably less than the gross temperature rise experimentally determined (Col. 9). The difference, Col. 13, is a measure of the heat of hydration of the $Cr_2O_7^=$ or step "a." The heat of hydration is then calculated from the concentration of $Cr_2O_7^=$ initially hydrated and the temperature difference given in Col. 13. The calculated values for this heat of hydration are given in Col. 15. The values for runs Ia and Ib are not in agreement with the remaining values and they have been omitted in determining the average value of −13,640 calories per mole of $Cr_2O_7^=$. The calculations of the heat of hydration are dependent upon a very small temperature increment, 0.020 and 0.018° for runs Ia and Ib, so a large experimental error is not required to alter these values greatly.

The heat effects for steps "a" + "b" + "c" and for step "a" have been computed from the experimental data. The value for step "c" has been well established as +13,700 calories per mole. The value for "b," the heat of dissociation of the $HCrO_4^-$ into H^+ and $CrO_4^=$, then becomes +780 calories per mole.

The neutralization of sodium dichromate has been assumed to be a pseudo-monomolecular reaction. If this assumption is correct, a straight line should be obtained when $\log a/(a - x)$ is plotted against time where a is the concentration of dichromate originally present and x is the concentration which has been neutralized at the time t. In this case the temperature change was used as a measure of a and x, the value of a being given in Col. 12. The data are represented in Fig. 5. The dichromate initially hydrated varied from 24.5 to 38% so the points do not give a single line but three lines. The intersection of these lines with the abscissa gives the correction to be applied for the construction of theoretical curves based on an initial condition of no hydration of the dichromate ion. The constants for

the reaction can be calculated from the corrected times and they are given in Table III. Values corresponding to the first six junctions are given, the sixth junction representing the reaction about 75% complete. Beyond

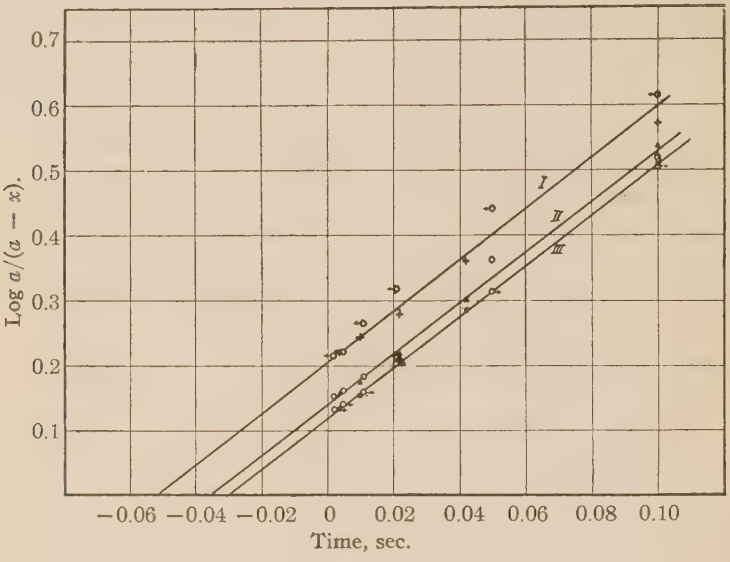


Fig. 5.

this point, a small error in the value of x has a very pronounced effect on the values ln $(a/a - x)$ and the results are not reliable. The average value for the constants for the seven experiments is 529.4 min.$^{-1}$.

TABLE III

MONOMOLECULAR CONSTANTS FOR THE NEUTRALIZATION OF $Cr_2O_7^=$ BY OH^- IN MIN.$^{-1}$

$k = 1/t \ln a/(a-x)$

Junction no.	Curve no. Ia	Ib	IIa	IIb	IIIa	IIIb	IV
1	524	534	549	553	529	562	556
2	495	516	517	546	522	542	543
3	507	567	520	541	535	520	532
4	518	602	528	518	539	539	436
5	498	576	545	582	538	535	490
6		553	486	526	459	542	527
Average	508	558	524	544	518	540	514

Average of all values, 529.4.

Theoretical curves for the neutralization of $Cr_2O_7^=$ by OH^- can be plotted by applying the time corrections obtained in Fig. 5 and the values for the neutralization had there been no initial hydration given in Col. 12. These curves are given in Fig. 6. The half time of 0.0785 second is obtained from the velocity constant.

7. Discussion of Results

Saal has studied the neutralization of potassium dichromate by sodium hydroxide by conductivity methods and on the basis of a very limited amount of data has concluded that the reaction is bimolecular. He considers the mechanism to be as follows

$$HCrO_4^- + OH^- \rightharpoonup CrO_4^= + H_2O$$
$$Cr_2O_7^= + OH^- \rightharpoonup CrO_4^= + HCrO_4^-$$

If this mechanism were correct, the reaction would probably be bimolecular but the rate of reaction would depend on the concentration of OH^- present. It has been shown that the concentration of OH^- has no effect on the rate of reaction. Saal's data are difficult to interpret and it is not possible to recalculate them on the basis of the reaction being monomolecular.

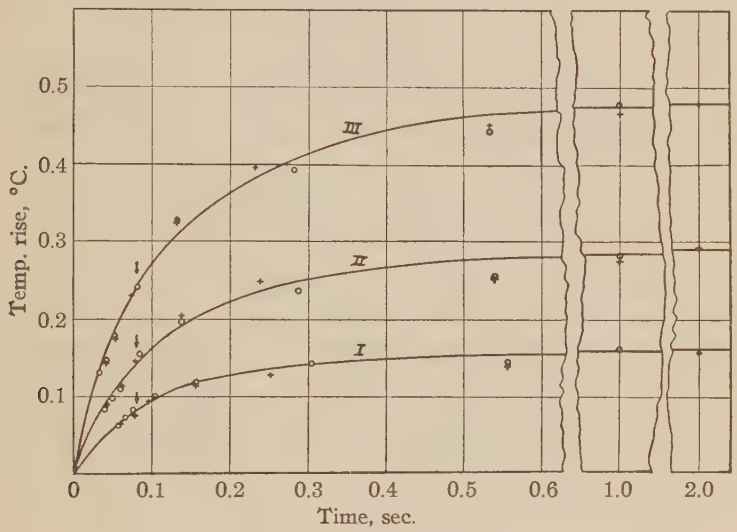


Fig. 6.—Theoretical curves.

Note of May 30, 1930.—Since this paper was submitted for publication, two recent papers by Roughton [*Proc. Roy. Soc.* (London), **A126,** 439, 470 (1930)] have come to our attention, in which the author has published the details of his thermocouple method of following chemical reactions to which he referred briefly in Ref. 3c. He gives an exhaustive analysis of the sources of error involved. Although Roughton's procedure for thermal control differs considerably from ours, he achieves a precision of 0.001° in the heats of neutralization. In the second paper he has studied some reactions of acids, bases and proteins in which the heats of reaction rather than the evaluation of the rate constants were of primary interest.

Acknowledgment.—We wish to express our indebtedness to Dr. J. W. Roughton for advice in the early stages of the investigation and to Mr. L.

J. Dornhofer, Chief Mechanician of the Laboratories, for the care which he exercised in constructing the Mixing Chamber.

Summary

1. An apparatus has been described for the study of rapid reactions, the progress of the reaction being followed by means of the temperature rise due to the heat of reaction evolved. The flowing stream method of Hartridge and Roughton has been employed, the reacting solutions being rapidly and completely mixed in a small mixing chamber and the resulting solution passed through a reaction tube at uniform velocity where the progress of the reaction is observed. The temperature rise between the point of mixing and any given point in the reaction tube was measured by thermocouples placed at measured intervals along the reaction tube, corresponding to time intervals which may be computed from the rate of flow.

2. The neutralization of $Na_2Cr_2O_7$ by sodium hydroxide has been studied at 25° with this apparatus. It has been shown that the following mechanism

(a) $Cr_2O_7^{=} + H_2O \rightleftharpoons 2HCrO_4^{-}$ (slow)
(b) $HCrO_4^{-} \rightleftharpoons H^+ + CrO_4^{=}$ (fast)
(c) $H^+ + OH^- \rightharpoonup H_2O$ (fast)

will account for the peculiarities of the reaction. Reaction "a" is pseudo-monomolecular with a half time of 0.0785 second and $k = 529$ reciprocal minutes. The heat of the gross reaction is +15,320 calories per mole of dichromate ion. The streaming method permits the determination of the heats of reaction involved in steps "a" and "b" which are not accessible by the usual methods. $q_a = -13{,}640$ calories per mole of $Cr_2O_7^{=}$ and $q_b = +780$ calories per mole of $HCrO_4^{-}$.

VITA

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